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Measurement of Neutral Sulfuric Acid-Dimethylamine Clusters using CI-APi-TOF-MS

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Abstract. Recent studies suggest that dimethylamine could be a key ternary species in the formation and early growth of atmospheric aerosol particles. We report on nucleation studies for the ternary system of sulfuric acid, water and dimethylamine which have been performed at the CERN CLOUD chamber. These studies were conducted at atmospherically relevant concentrations of sulfuric acid and dimethylamine at 278 K and 38% RH. Two newly developed Chemical Ionization-Atmospheric Pressure interface-Time of Flight-Mass Spectrometers (CI-APi-TOF-MS) were used to measure the time-resolved concentration of neutral clusters containing sulfuric acid and dimethylamine. Results from other instrumental techniques are included in the analysis as well to obtain a deeper insight into the occurring mechanisms. It is the first time that the neutral nucleation pathway has been studied in such detail from the early generation of sulfuric acid monomers up to particle sizes reaching several nanometers.

Keywords: Chamber study, CLOUD experiment, Ternary Nucleation, Amines.
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TERNARY H_2SO_4-H_2O-DIMETHYLAMINE NUCLEATION

Aerosol particles have a substantial impact on the Earth's climate by scattering or absorbing solar and terrestrial radiation and their ability to act as Cloud Condensation Nuclei (CCN) or Ice Nuclei (IN). Model calculations suggest that about half of the airborne particles could originate from nucleation[1]. However, the uncertainty in this number is large and it is still unclear which vapors are participating in the formation of the critical nucleus under certain conditions and which species contribute to its early growth. In most cases atmospheric boundary layer nucleation events cannot be explained solely by the binary system of sulfuric acid and water, although a correlation with the sulfuric acid concentration is generally observed[2,3]. Consequently, ternary vapors need to participate and it has been suggested that ammonia plays a key role[4,5]. Recently, a chamber study has shown that the addition of ammonia to the binary system can enhance the nucleation rates substantially[6]. However, even the

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ternary system involving NH_3 is not sufficient to explain the high nucleation rates which are frequently observed in the boundary layer.

Kirkby et al. have shown that in the ternary NH_3 system the nucleating clusters grow in a stepwise process. This growth proceeds either by adding ammoniumbisulfate molecules or a sulfuric acid monomer followed by a rapid addition of an ammonia molecule which helps to stabilize the cluster through a so-called "acid-base-stabilization" mechanism[6]. This observation suggests that compounds which have a stronger basicity than ammonia could enhance the nucleation rates further. Such compounds could be amines of which a huge variety has been identified in the atmosphere[7]. Amines have already been predicted as likely candidates enhancing the nucleation rates based on quantum-chemical studies[8,9] and it has been observed that they contribute in the formation of secondary aerosol[10,11]. Laboratory studies as well as atmospheric measurements have also revealed that amines enhance ternary nucleation[12-14]. In addition, a recent CLOUD (Cosmics Leaving OUtdoor Droplets) chamber study was able to show that the ternary H_2SO_4-H_2O-DMA (DMA, dimethylamine, $(CH_3)_2NH$) system can explain atmospheric boundary layer nucleation events for atmospherically relevant concentration of sulfuric acid and dimethylamine under certain conditions[15].

Measurements suggest that atmospheric boundary layer nucleation proceeds mainly via a neutral process and ion-induced nucleation usually plays only a minor role[16]. Therefore, it is of importance to study the neutral pathway. The instrumentation which is necessary to measure the concentration of neutral clusters and to identify them unambiguously has only emerged very recently. The Chemical Ionization-Atmospheric Pressure interface-Time Of Flight (CI-APi-TOF)[17] mass spectrometer allows studying the molecular mechanisms underlying the neutral nucleation process. Among other instruments, two CI-APi-TOFs have been used to investigate the DMA ternary system in a recent CLOUD experiment.

EXPERIMENTAL METHODS

The results reported were obtained from measurements at the CERN CLOUD chamber in fall 2012 (CLOUD7 campaign). The CLOUD chamber allows studying the effect of ions on nucleation and their activation to cloud droplets or ice particles[6]. A high voltage clearing field installed inside the chamber can be used to effectively remove ions and charged particles, thereby allowing the investigation of the pure neutral nucleation pathway. Besides this unique feature, one other important characteristic of CLOUD is the suppression of contaminants at the technological limit. The extremely sensitive instrumentation used at CLOUD allows the identification of potential contaminants and to measure their concentration above a certain limit. These combined features make the conducted experiments very well controlled and therefore allow the investigation of the effect of dimethylamine on the ternary nucleation.

Sulfuric acid being one of the key compounds relevant for the nucleation is produced in-situ by illuminating the gas inside the chamber homogenously with UV light. The concentration of the sulfuric acid monomer is routinely measured with a Chemical Ionization Mass Spectrometer (CIMS) during the different CLOUD

campaigns[18]. Dimethylamine diluted in nitrogen from a gas bottle was injected into the chamber after further dilution with nitrogen to achieve the desired concentrations. The injection was performed close to a magnetically driven mixing fan made of stainless steel. Therefore, a homogenous mixture of sulfuric acid and dimethylamine was rapidly achieved while the concentration of dimethylamine was monitored with an ion chromatograph[19]. Typical measured concentrations were between ~3 and ~40 pptv when DMA was added to the chamber.

Two Chemical Ionization-Atmospheric Pressure interface-Time Of Flight (CI-APi-TOF) mass spectrometers were operated at the CLOUD chamber for the first time during CLOUD7. The CI-APi-TOFs use the same method as the CIMS for the ionization of neutral species. Nitrate ions generated in an ion source can react with molecules and clusters in a drift tube. However, in contrast to the linear quadrupole mass filter used for the CIMS, the CI-APi-TOFs utilize a high resolution time-of-flight mass spectrometer[17]. This has several important advantages: (i) a large mass range up to ~2000 Th, therefore allowing the detection of large clusters, (ii) chemical identification of the ionized species including separation of ions with identical integer mass but different atomic mass defects, and (iii) high sensitivity. The two CI-APi-TOFs differ in some experimental details, e.g. with respect to their effective reaction time inside the ion drift tube and the voltage settings of the mass spectrometer and its ion guides. However, despite these differences a remarkably good overall agreement between the two instruments was found.

DISCUSSION

The two CI-APi-TOFs were used to detect neutral clusters containing sulfuric acid and dimethylamine. The exact composition of such clusters can be unambiguously identified due to the high resolution and accuracy of the mass spectrometer. The time dependency of the concentrations of clusters with different size can be used to derive the cluster growth rates. Comparison with model results can further be performed to gain insight about the growth and the potential evaporation or fission of clusters. Finally, an integrated analysis involving further instruments using condensation techniques for the detection of particles as small as 1 nm allows the description of the nucleation process from the very first step, i.e. the photolytic generation of sulfuric acid monomers, up to a particle size of several nanometers. Such a complete set of measurements has been performed for the very first time and yield a great step towards a more complete understanding of nucleation.

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REFERENCES

1. J. Merikanto et al., *Atmos. Chem. Phys.* **9**, 8601–8616, (2009).
2. S.-L. Sihto et al., *Atmos. Chem. Phys.* **6**, 4079–4091 (2006).
3. C. Kuang et al., *J. Geophys. Res.* **113**, D10209, doi:10.1029/2007JD009253 (2008).
4. S. M. Ball et al., *J. Geophys. Res.* **104**, D19, 23,709–23,718 (1999).
5. P. Korhonen et al., *J. Geophys. Res.* **104**, D21, 26,349–26,353 (1999).
6. J. Kirkby et al., *Nature* **476**, 429–433 (2011).
7. X. Ge et al., *Atmos. Env.* **45**, 524–546 (2011).
8. T. Kurtén et al., *Atmos. Chem. Phys.* **8**, 4095–4103, (2008).
9. I. K. Ortega et al., *Atmos. Chem. Phys.* **12**, 225–235 (2012).
10. S. M. Murphy et al., *Atmos. Chem. Phys.* **7**, 2313–2337 (2007).
11. J. N. Smith et al., *Proc. Natl. Acad. Sci*. **107**, 15, 6634–6639 (2010).
12. J. H. Zollner et al., *Atmos. Chem. Phys.* **12**, 4399–4411 (2012).
13. H. Yu et al., *J. Geophys. Res.* **39**, L02807, doi:10.1029/2011GL050099 (2012).
14. M. Chen et al., *Proc. Natl. Acad. Sci*., doi/10.1073/pnas.1210285109 (2012).
15. J. Almeida et al., *in prep.* (2013).
16. V.-M. Kerminen et al., *Atmos. Chem. Phys.* **10**, 10829–10848 (2010).
17. T. Jokinen et al., *Atmos. Chem. Phys.* **12**, 4117–4125 (2012).
18. A. Kürten et al., *Atmos. Meas. Tech.* **4**, 437–443 (2011).
19. A. P. Praplan et al., *Atmos. Meas. Tech.* **5**, 2161–2167 (2012).